

# **COAL BLENDING, ASH SEPARATION, ASH RE-INJECTION, ASH CONDITIONING, AND OTHER NOVEL APPROACHES TO ENHANCE HG UPTAKE BY ASH IN COAL-FIRED ELECTRIC POWER STATIONS**

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## **ABSTRACT**

Differences in coal type and pollution control devices make it necessary to develop customized solutions for each utility, which will be most effective and economical for each configuration. In addition, the complicated chemistry and multiple mechanisms governing mercury speciation in coal-fired boilers makes it necessary to investigate Hg emission control technologies at conditions relevant to full-scale units. Experiments were performed in a 1MW(Th) semi-industrial scale coal-fired facility, representative of a full-scale boiler. State-of-the-art mercury measurement capabilities enabled Hg-speciation measurements with less than 5% uncertainty in the measured values. An understanding of the mechanisms governing Hg speciation in coal-fired boilers has been elucidated through this research, thus enabling manipulation of parameters to significantly enhance Hg uptake by ash. Mercury mitigation solutions for a variety of different power-plant configurations are presented, including those burning either Powder River Basin (PRB) sub-bituminous or Eastern bituminous coal. Of particular mention, it was shown that unburned carbon in ash, manipulated either through coal blending or through combustion modifications, enhanced Hg capture by calcium. Ash conditioning results were promising for mercury removal across the air heater, and ~10-ppmv of Na<sub>2</sub>S<sub>4</sub> was sufficient to remove all of the mercury from low-chlorine (i.e., PRB) flue gas.

## **INTRODUCTION**

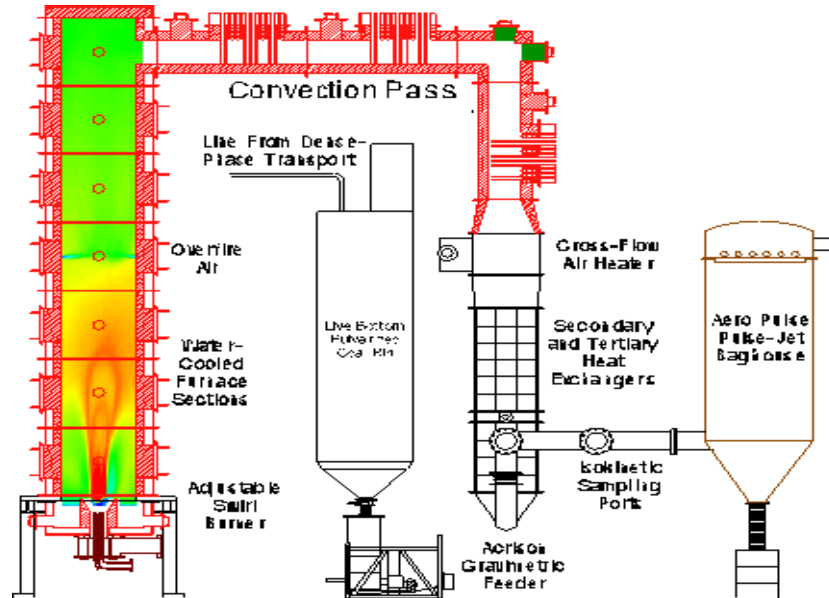
Extensive research at Southern Research Institute has been conducted to gain an understanding of mercury speciation in coal-fired boilers<sup>1-5</sup>. The major mechanisms governing mercury speciation in coal-fired boilers have been elucidated, leading directly to Hg emission control strategies for a variety of different utilities.

Control options for mercury mitigation need to be utility specific, because the dominant mechanism governing mercury speciation differs from one plant to another. The parameters of importance include coal type (i.e., PRB, lignite, bituminous), particulate control device (i.e., cold-side ESP, hot-side ESP, WESP, baghouse), NO<sub>x</sub> control (i.e., SCR, low-NO<sub>x</sub> burners, reburning), and SO<sub>x</sub> control (i.e., wet and dry scrubbers). Results relevant to a variety of different configurations are presented here. Technologies investigated include coal

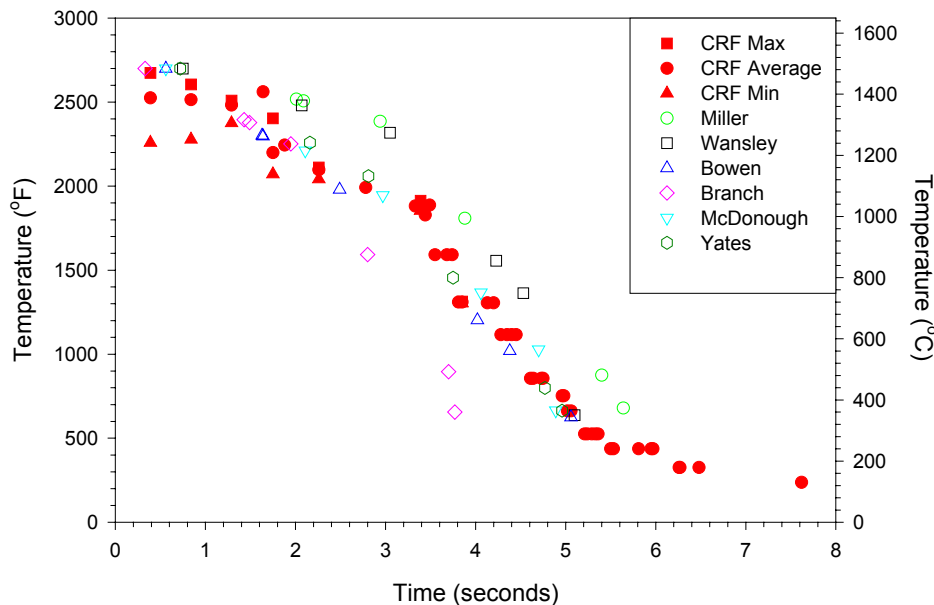
blending, ash conditioning, combustion modifications, catalytically enhanced mercury capture, and direct removal of both elemental and oxidized mercury through sodium tetrasulfide injection.

## EXPERIMENTAL

The Combustion Research Facility (CRF) at Southern Research Institute (SRI) in Birmingham, AL, is a 1-MW<sub>t</sub> semi-industrial-scale, coal-fired facility, which mimics the conditions in a full-scale boiler. Figure 1 shows a two-dimensional sketch of this facility.



**Figure 1.** Combustion Research Facility (CRF).



**Figure 2.** Combustion Research Facility (CRF) temperature/time histories compared with those of full-scale Southern Company coal-fired power plants.

The Aero-Pulse pulse-jet baghouse uses full-scale Ryton-bags. As shown in Fig. 2, the temperature/time history of the CRF mimics that of full-scale power plants from the burner through the economizer. Two different baghouse temperature conditions were explored, a high (Inlet = 337 °F Outlet = 300 °F) and a low (Inlet = 280 °F Outlet = 260 °F) condition. The baghouse temperature was adjusted by changing the rate of cooling in the last set of heat exchangers, the inlet temperature of which was fairly constant and was always below 550 °F. Several hours were allowed between each change in baghouse temperature to allow the system to reach steady state.

An extractive, continuous-emissions-monitoring (CEM) system measured the concentrations of CO, CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, and O<sub>2</sub> in the flue gas, just ahead of the baghouse. In addition, manual measurements of chlorine and moisture were obtained throughout the testing.

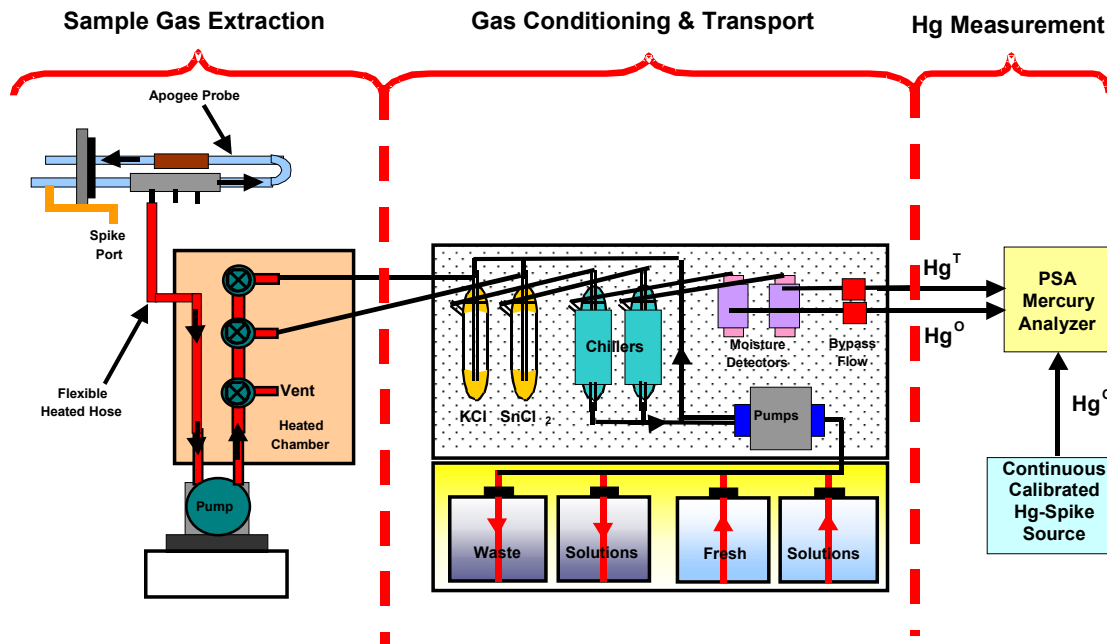
Mercury monitoring was performed with an advanced and improved version of the PS Analytical 10.665 Stack Gas Analyzer. The PSA monitor used in this investigation was customized by SRI with an APOGEE Scientific QGIS probe. The QGIS probe is designed to pull a large volume of flue gas into and through the annulus of a metal tube at a high and turbulent velocity, thus scouring the walls of the tube clean. A section of the annulus is a sintered-metal porous frit through which a small sample of flue gas is drawn.

The excess flue gas is directed back into the duct, downstream of the sample inlet. In this way, the QGIS probe allows a sample to be drawn from the duct without pulling it through an ash layer, thereby minimizing alteration of the gas sample – especially capture or oxidation of the vapor-phase mercury by or on the particulate. Southern Research also developed an advanced *continuous spike and recovery* system to validate the correctness of the mercury-speciation numbers measured and correct for errors that occur. As a result of these and other modifications, Southern Research Institute was able to measure mercury speciation within a maximum uncertainty of 5%. Accurate and precise mercury speciation measurements are key to a fundamental mercury speciation and capture investigation.

The *continuous calibrated spike-generation system* is a first of its kind prototype provided by PS Analytical. The adaptation of this system to allow spiking at the tip of the APOGEE Scientific QGIS probe with minimal dilution of the sample gas was performed by Southern Research personnel. The spike of mercury is introduced into the tip of the APOGEE Scientific QGIS probe far enough downstream from the inlet to prevent losses to the duct and far enough upstream of the porous annulus to allow complete mixing before the sampled gas is pulled through the porous frit. A relatively small quantity of air is used to carry the mercury spike to the probe. Therefore, dilution is insignificant, and the general flue-gas composition is undisturbed.

The main effect of the spike is simply to increase the concentration of mercury in the sampled gas. This is significant, since mercury-oxidation processes that interfere with speciation measurements can involve three- and four-component interactions of flue-gas species on catalytic ash sites<sup>6</sup>. The concentration of mercury in the spike stream is generated by controlling the flow rate, pressure, and temperature of air in and through a mercury reservoir chamber. In addition, SRI uses a parallel Hg source for the *spike and recovery*

system, involving permeation tubes, allowing a check on the source calibration. High-precision mass flow controllers are used to obtain the precise metering needed for high-certainty calibrated spikes. Southern Research believes that *continuous spike and recovery* provides a greater level of confidence in the resulting mercury speciation than any other method currently in use. A schematic of the monitoring system is presented in Fig. 3, including spike location, gas-conditioning system, and continuous calibrated-spike source.

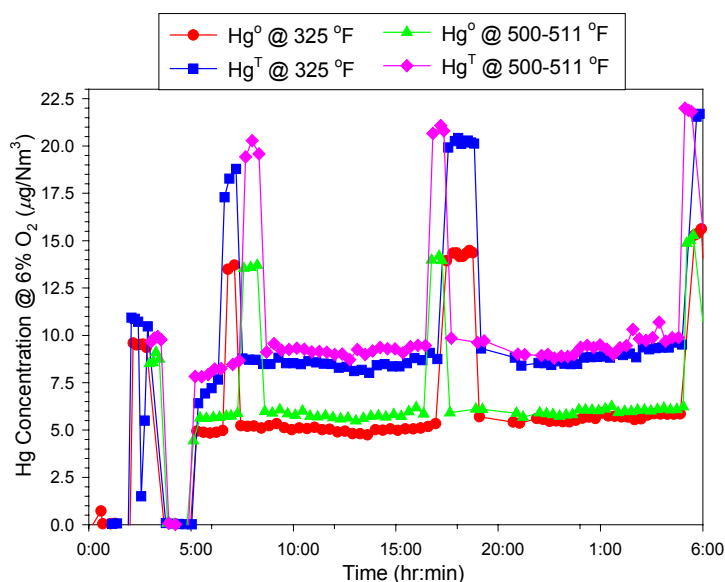


**Figure 3.** Mercury monitoring system, including continuous spike and recovery.

Figure 4 illustrates the use of the continuous spike and recovery system for establishing total and oxidized mercury concentrations in the flue gas, while first burning natural gas (time 0:00 to 5:00) and then Black Thunder, a Powder River Basin (PRB) coal. As shown, the *spike recoveries* are observed on top of the measured initial mercury concentrations for both fuels. The mercury speciation data were obtained well upstream of the baghouse.

The *continuous spike and recovery system* allows systematic errors to be observed and corrected as long as the spike recoveries are within 20% of the expected value.

Black Thunder Powder River Basin Coal (PRB) and two bituminous coals, Choctaw America and Blacksville, were used in this work. The PRB coal is the same coal used to obtain the data in Fig. 4. Both PRB and Choctaw America are low-chlorine coals. Blacksville is a moderate-chlorine coal. Analyses of these coals can be found elsewhere<sup>1-3</sup>.



**Figure 4.** Mercury speciation data taken with an advanced and customized Hg-speciation SCEM, and validated with *continuous spike and recovery* for quality assurance.

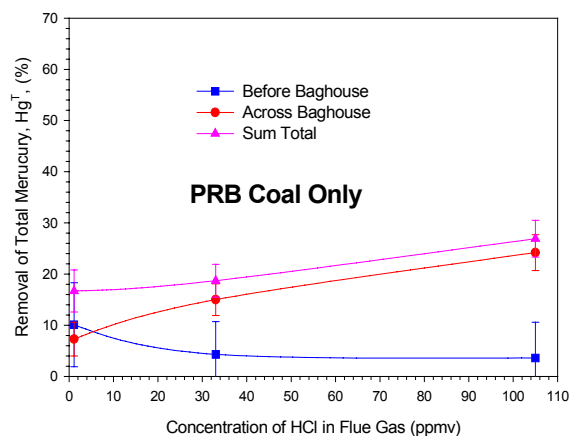
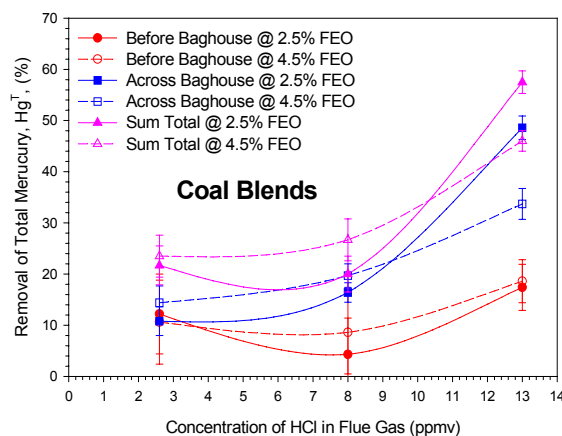
## RESULTS AND DISCUSSION

### Coal Blending

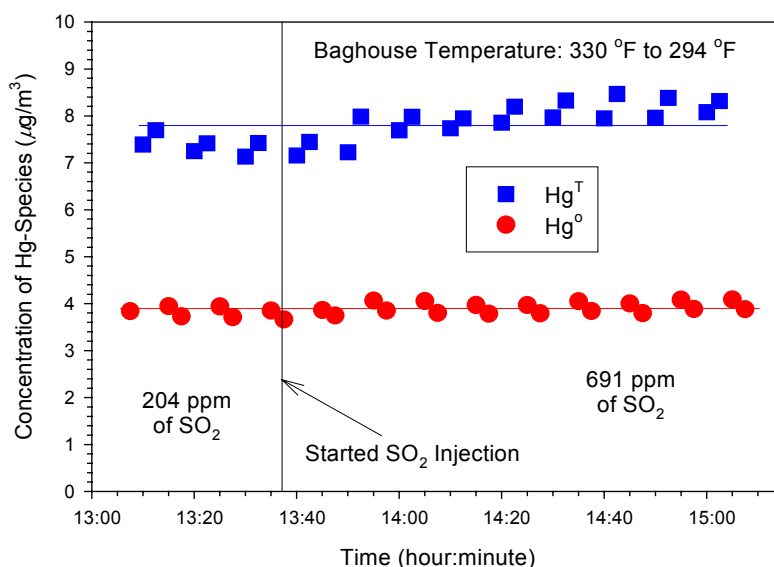
The combustion products of most coals do not contain the complete set of components needed to effectively remove mercury from the flue gas. In addition to chlorine content, the composition of the ash is very important. As presented elsewhere<sup>2,4</sup>, both unburned carbon (UBC) and calcium are necessary ash components for reactive capture of mercury by flyash. The UBC in ash catalytically enhances the oxidation of elemental mercury to  $\text{HgCl}_2$ <sup>1-4</sup> and its subsequent reactive capture by calcium in the ash. The calcium in the ash acts as the sorbent material, which reactively scavenges the oxidized mercury<sup>5</sup>.

Figure 5 illustrates the benefits of blending PRB sub-bituminous coal with bituminous coals to combine both the catalytic material (UBC) and sorbent material (calcium) to enhance mercury capture by the flyash. Figure 6 illustrates the ineffectiveness of chlorine injection alone at increasing mercury capture by PRB flyash. Catalytic material in the form of UBC is more important to the enhancement of mercury capture by flyash than the increase of total chlorine content. Comparing the scale differences in Figs. 5 and 6, it is observed that Hg-removal enhancement through coal blending generated significant capture at relatively little chlorine.

An exploration of Hg-oxidation and Hg-capture correlations with each parameter affected by coal blending, revealed that flue gas components other than chlorine had little effect<sup>1-4</sup>. For example, Fig. 7 shows the results of isolating the effect of  $\text{SO}_2$  concentration while burning PRB coal. Even though the concentration of  $\text{SO}_2$  was increased by nearly 500 ppm, there was little or no effect on mercury oxidation or capture.



**Figure 5.** Hg-removal through coal blending. **Figure 6.** Hg-removal through HCl injection.

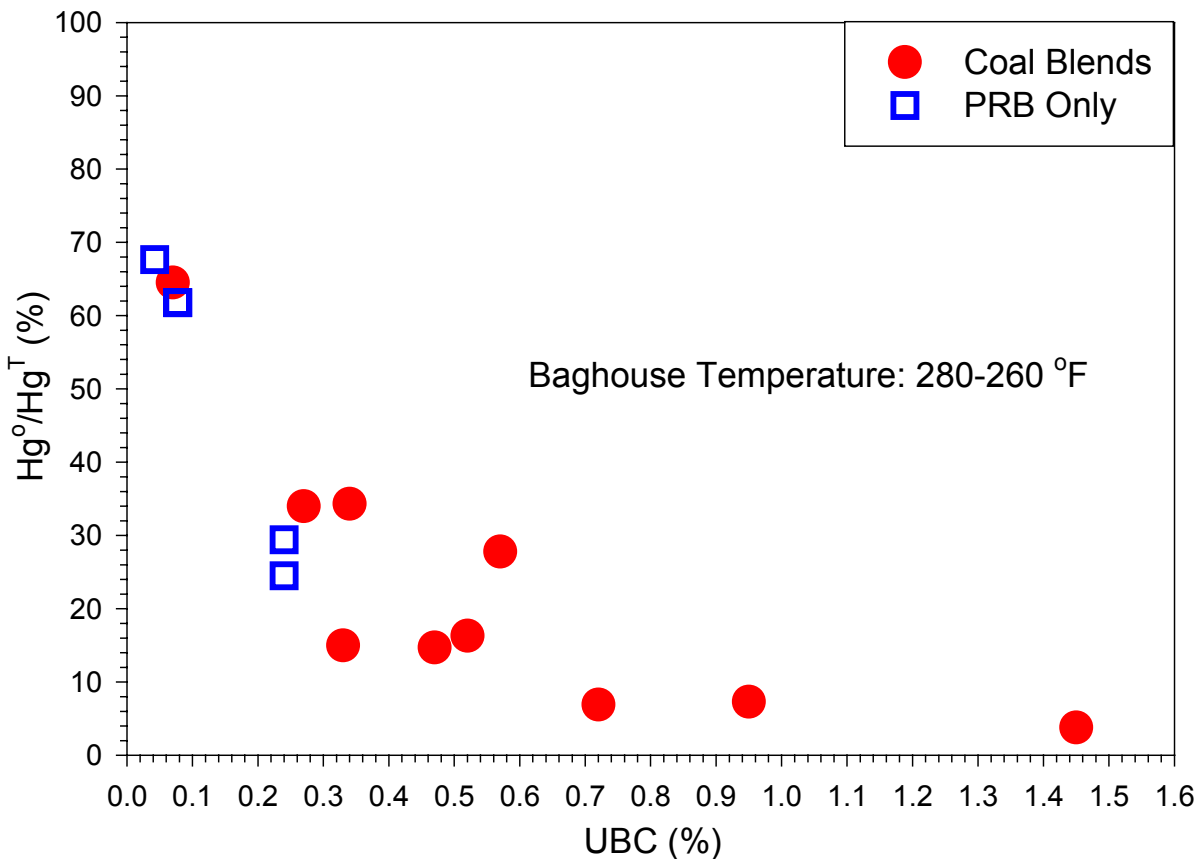


**Figure 7.** Effects of SO<sub>2</sub> injection on Hg-speciation, while firing PRB coal.

As illustrated in Fig. 8, the dominant parameter of importance to enhanced mercury oxidation through coal blending is the UBC in ash. The coal-blending data points indeed indicate a decreasing relationship between the fraction of elemental mercury in the flue gas and UBC in the ash, increased by blending 10 to 20% bituminous coal with the PRB coal. However, mineral matter in the ash also increased along with UBC for coal blending. In order to isolate the effects of UBC on Hg oxidation, combustion modifications were used to increase the UBC while burning PRB coal only. Combustion in the furnace was modified so as to increase the UBC from coal char and avoid generating soot, which would have different properties than typical UBC. Specifically, the airflow and swirl at the burner were maintained, so as to continue to consume the volatiles and prevent the formation of soot. Char UBC was increased by lowering the airflow and reducing the swirl through the overfire-air ports such that the furnace exit oxygen was lower and char burnout was less efficient.

The results of the UBC isolation tests are shown in Fig. 8. The mercury oxidation increase from coal blending is completely accounted for by the addition of UBC to the flyash. As

shown, UBC is the dominant parameter affecting flue-gas Hg-oxidation-state differences between PRB sub-bituminous and bituminous coal-fired power plants.

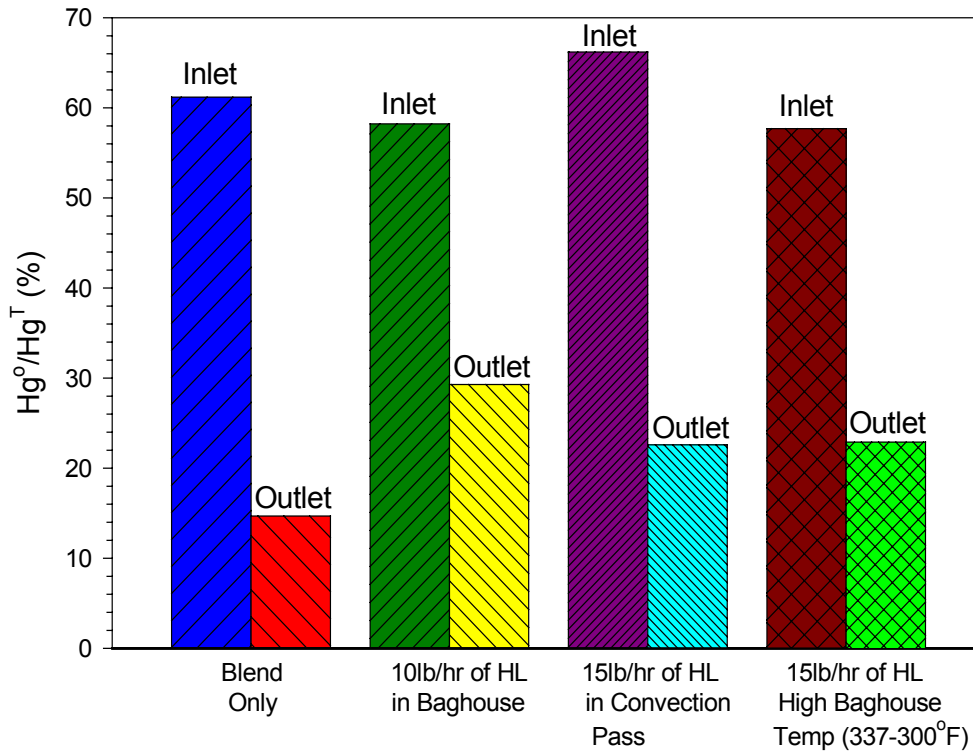


**Figure 8.** Mercury oxidation correlation with UBC for PRB and coal blends.

### Ash Separation

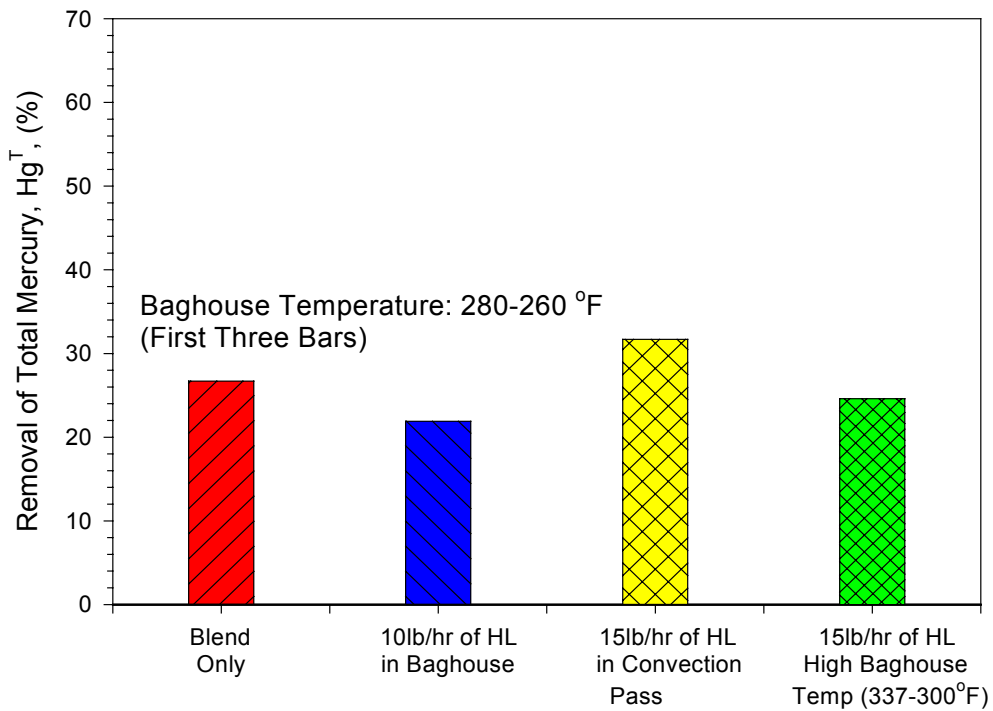
Primarily as a means of maintaining ash quality and marketability, processes have been developed and demonstrated that allow sorbent injection independent of flyash collection. Examples include the EPRI patented processes COHPAC-I and COHPAC-II. Activated carbon, while effective at removing mercury across a baghouse, will contaminate ash otherwise marketable as an additive for cement production. Activated carbon as a physical sorbent has been advocated for mercury removal in coal-fired power plants. However, calcium chemisorbents may be more effective, cost efficient, and less detrimental to ash sales. In the case of calcium-based sorbents however, carbon material is needed as a catalyst, in addition to the calcium sorbent. Hence, ash separation may in some cases be detrimental to the effectiveness of calcium-based sorbents on mercury removal.

Figures 9a and 9b illustrate the ineffectiveness of hydrated lime at removing mercury when injected into a baghouse during coal blending. As shown in Fig. 9a, the coal blend did not produce significant Hg oxidation at the baghouse inlet. Approximately 80% of the mercury was oxidized by the time the flue gas exited the baghouse. Nevertheless, hydrated lime



Hydrated Lime (HL) Injection Condition

**Figure 9a.** Hg oxidation at the inlet and outlet of the baghouse.

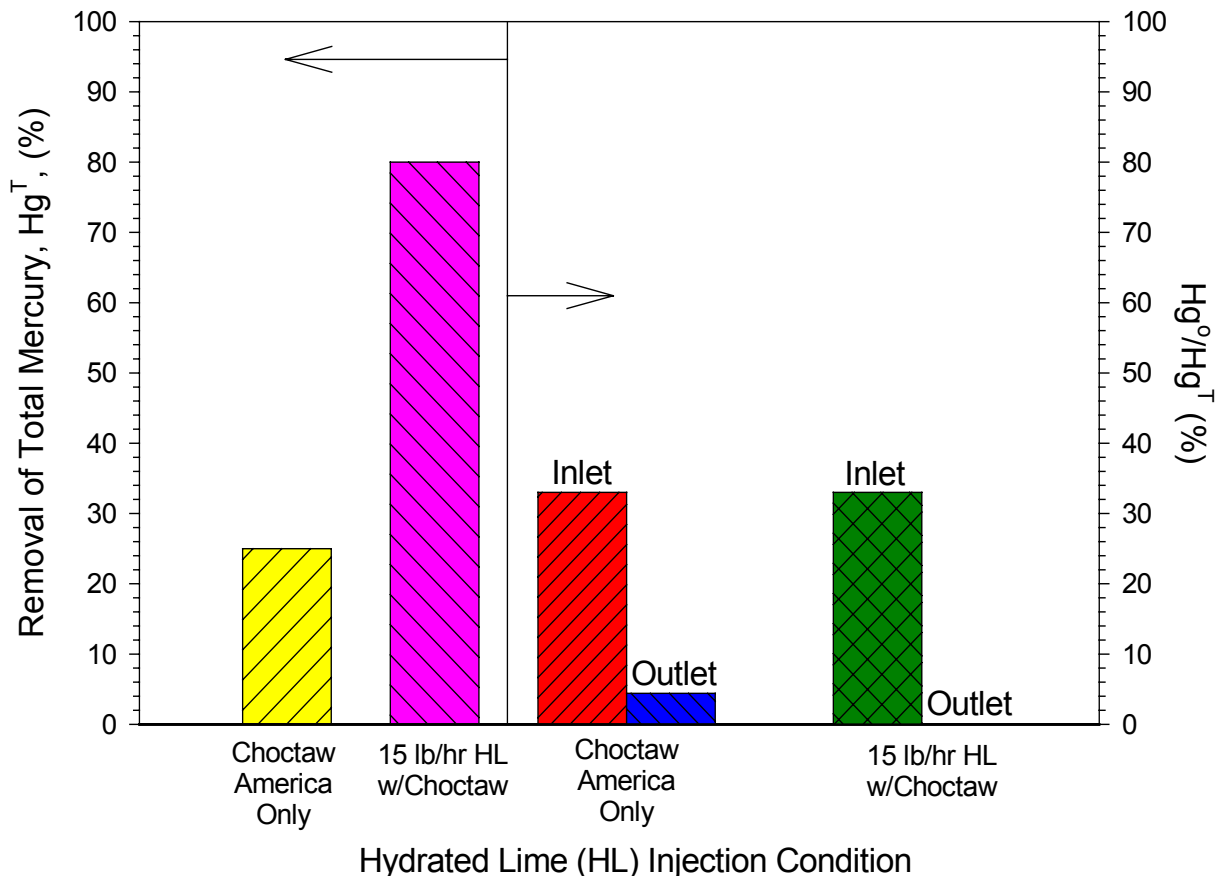


Hydrated Lime (HL) Injection Condition

**Figure 9b.** Hg removal at the baghouse outlet.



injection into the baghouse did little to improve mercury capture (see Fig. 9b). The ash from the coal blend contained sufficient catalytic material to enhance Hg oxidation across the filter cake, but more catalytic material was needed to enhance Hg capture across the baghouse. Figure 10 illustrates the effectiveness of hydrated lime ( $\text{Ca}(\text{OH})_2$ ) as a Hg sorbent when firing a low-chlorine bituminous coal (~3.5% UBC in the ash). As shown, only about 25% of the mercury was removed while burning Choctaw America coal without sorbent injection. However, hydrated lime injection into the baghouse increased Hg removal up to nearly 80%. Thus, hydrated lime and calcium in general can be effective sorbents if mixed with the necessary catalytic material.



**Figure 10.** Hg removal while burning bituminous coal and injecting hydrated lime.

### Ash Re-Injection

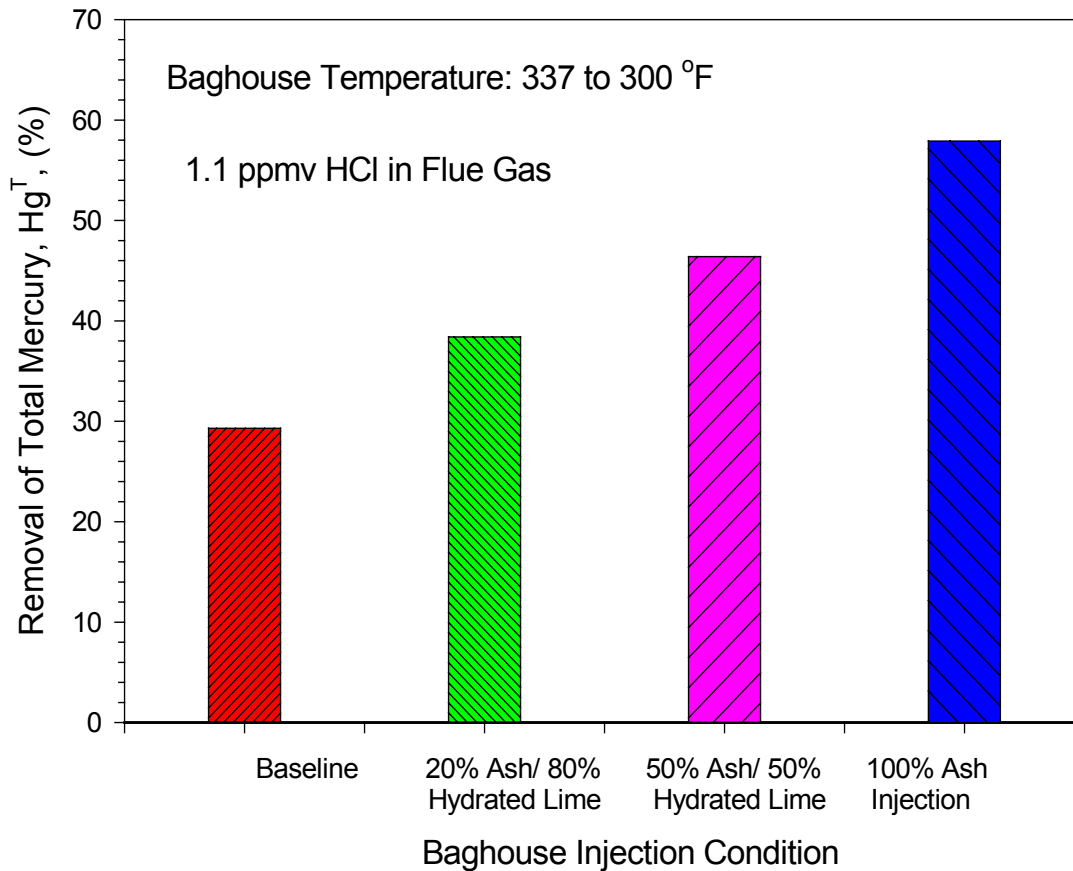
One approach to combining the ash components necessary to promote mercury removal is to inject ash of one coal type into the baghouse of a power plant that burns another coal type. Either a high calcium ash (i.e., PRB) may be injected into the baghouse of a power plant burning a coal with significant catalytic material (i.e., UBC) or a bituminous ash may be injected into the baghouse of a plant burning a high-calcium coal. The latter was attempted in this investigation. Ash collected in the CRF from burning Choctaw America, a low-chlorine bituminous coal, was collected and later re-injected into the baghouse while firing PRB sub-bituminous coal. Table 1 contains the analysis of the ash injected. The Choctaw America ash was fairly low in calcium and had a UBC of ~3.5%.

**Table 1.** Analysis of Choctaw America coal ash injected into baghouse.

Mineral Analysis		Other Properties	
% Li <sub>2</sub> O	0.06	LOI	4.2 %
% Na <sub>2</sub> O	1.4	UBC	3.51 %
% K <sub>2</sub> O	2.0		
% MgO	1.2		
% CaO	3.9		
% Fe <sub>2</sub> O <sub>3</sub>	12.4	meso-pore N <sub>2</sub> -BET Surface Area	2.32 m <sup>2</sup> /g
% Al <sub>2</sub> O <sub>3</sub>	33.0		
% SiO <sub>2</sub>	43.1		
% TiO <sub>2</sub>	1.8		
% P <sub>2</sub> O <sub>5</sub>	0.38	<i>PRB Ash</i> <i>Surface Area</i>	<i>PRB Ash</i> <i>2.02 m<sup>2</sup>/g</i>
% SO <sub>3</sub>	0.53		

LOI = Loss On Ignition, UBC = Unburned Carbon

The surface area of the injected ash was similar to that of the PRB ash produced in the furnace. Figure 11 illustrates the results of injecting the Choctaw America coal ash (see Table 1) into the baghouse while burning PRB coal in the CRF. In addition to 100% flyash, several mixtures of hydrated lime and ash were injected into the baghouse.

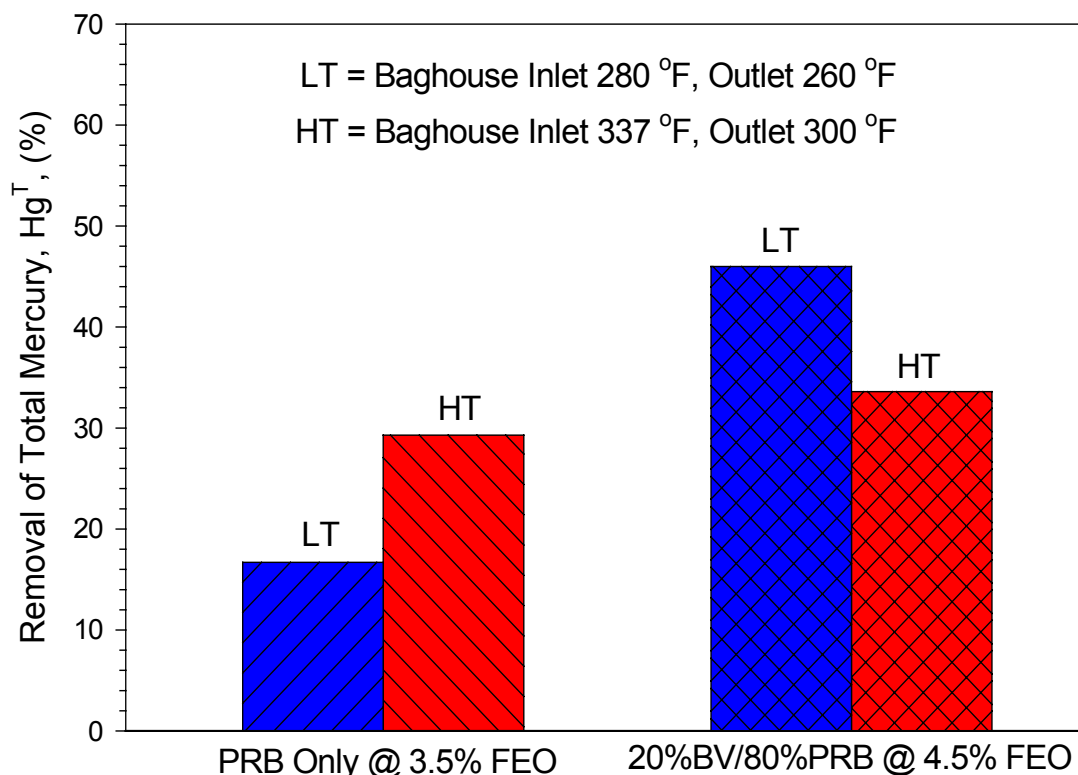


**Figure 11.** Effect of Ash Re-Injection on Hg removal.

The injection rate of material was approximately equal to half that of the ash loading from the duct and was consistent for all three injection conditions shown in Fig. 11. Mercury removal increased with increasing bituminous ash concentration, achieving twice the total removal of the baseline condition while injecting 100% bituminous ash.

Hydrated lime has approximately an order of magnitude higher internal surface area than coal ash. Nevertheless, the hydrated lime appeared to have little effect on mercury removal in the baghouse other than to dilute the concentration of bituminous ash being injected. This is reasonable, since the PRB ash itself contained sufficient calcium to capture the mercury if enough catalytic material were present. The bituminous ash being injected contained the needed catalytic material to enhance Hg capture. Hence, it is the catalytic material (i.e., UBC) in the bituminous ash that enhanced Hg capture by calcium, not just the increased surface area.

The increase in mercury removal illustrated in Fig. 11 was performed at an elevated baghouse temperature (337 to 300 °F). Had the demonstration been performed at a lower, more common baghouse temperature (280 to 260 °F), the impact of ash re-injection would have been much more significant. Figure 12 illustrates that the higher-temperature baghouse condition was more favorable to Hg removal with PRB only, while the lower-temperature condition was more favorable for the coal blends.



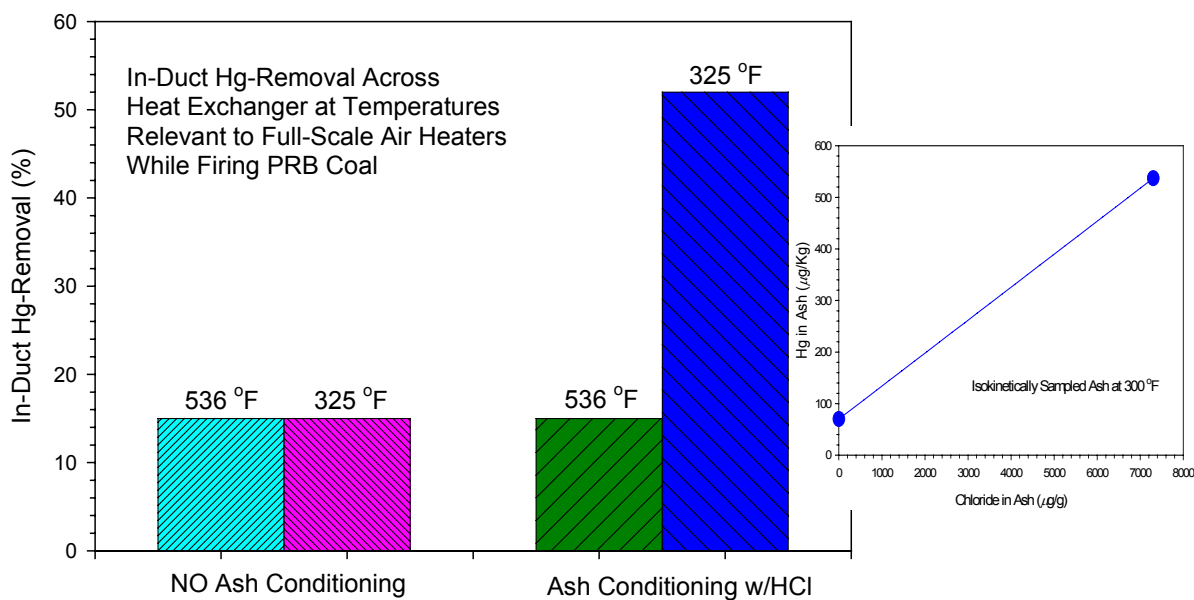
**Figure 12.** Baghouse temperature dependence of Hg removal.

The temperature dependence in Fig. 12 also illustrates that Hg removal for low-UBC PRB coal conditions is governed by a different set of mechanisms than governs in bituminous coal-fired conditions. There are other flyash components that catalytically promote the

oxidation of mercury, including calcium, iron, and titanium. However, the catalytic effects of UBC dominate over the catalytic activity of other materials for UBC levels above ~0.1%. The kinetic relationships of the governing catalytic reactions for very low UBC PRB-fired conditions are such that the higher temperature was more effective. When the UBC level increased, the governing mechanism changed to that of UBC catalytic enhancement, which was more favorable at the low-temperature condition.

## Ash Conditioning

The effect of ash conditioning on mercury removal was examined in the CRF at SRI. Hydrochloric acid generated by injecting chlorine through the burner was found to be an effective ash conditioner for enhancing the in-flight Hg uptake by PRB flyash. However, ash conditioning was only beneficial in the duct and heat exchangers between 536 °F and 325 °F, in the temperature range of full-scale Lungstrum air heaters.



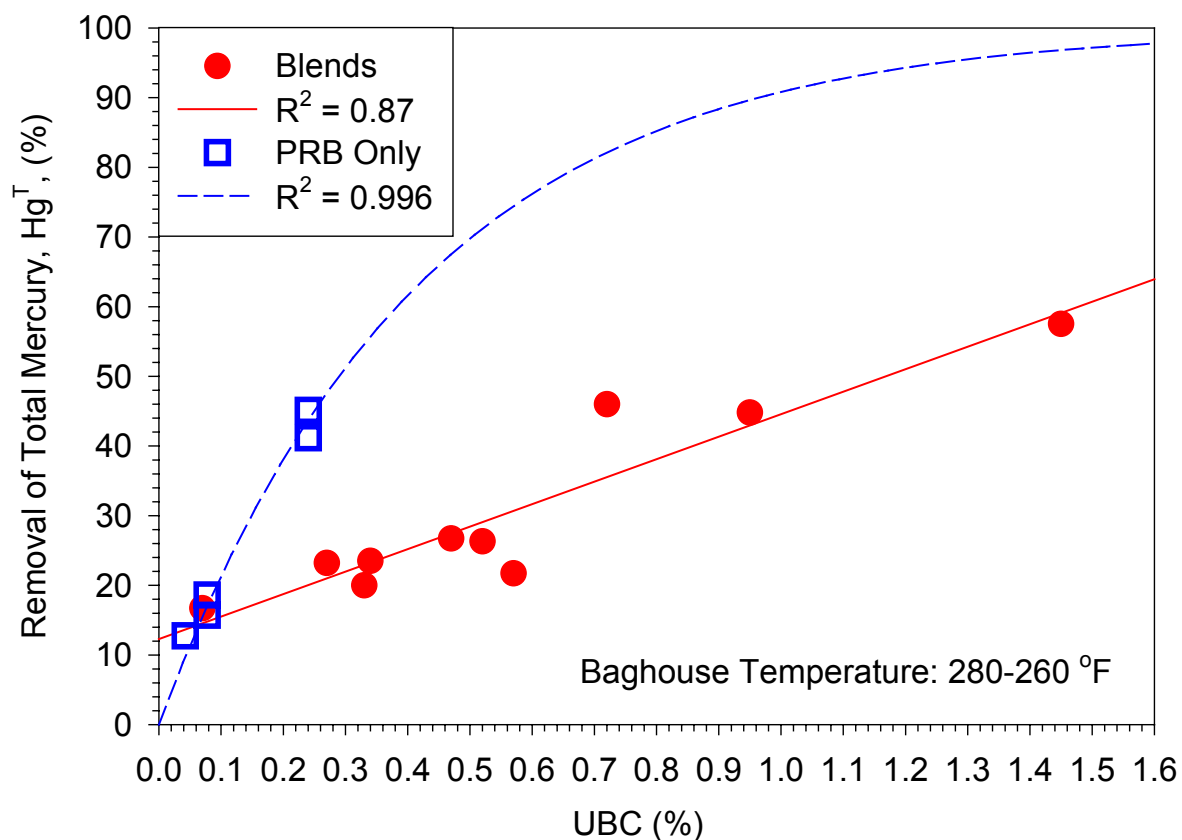
**Figure 13.** Effects of ash conditioning on Hg-removal.

As shown in Fig. 13, mercury removal across the low temperature heat exchanger was increased from ~15% to ~50% through ash conditioning. No special attempt was made in this test to optimize the ash conditioning process. Optimized ash conditioning agents, engineered conditioning processes, and customized strategies will allow much more effective disperse-phase mercury removal than herein observed. To the right of the bar graph in Fig. 13 is a graph showing the relationship between chloride in the ash and mercury in the ash, analyzed from isokinetically sampled ash during the ash-conditioning test. As shown, ash with high chloride content also contained high mercury content.

## Combustion Modifications

As discussed in a previous section, coal blending enhances the capture of mercury by flyash by combining necessary catalytic material (UBC) with sorbent material (calcium). However, coal blending also includes material that is superfluous to the process. Figure 14 illustrates the relationship between mercury removal and UBC for data taken while blending 20% or less of two different bituminous coals with PRB coal. The far left data point is for PRB-only, which coincides with repeat data for PRB-only taken several months later, during a combustion modification test. Combustion modifications are a way to increase UBC in ash for high-calcium coals without adding the unnecessary supplemental material introduced by blending with bituminous coal.

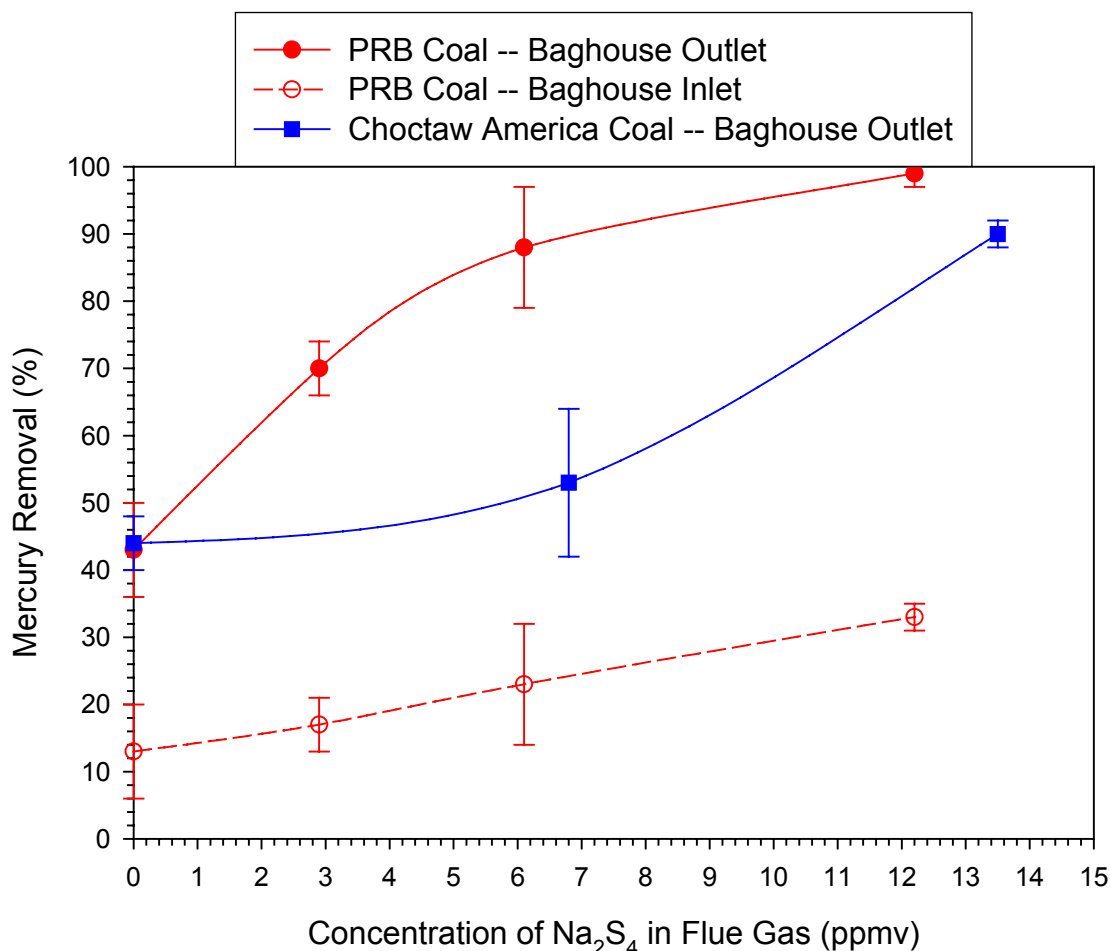
The increase of mercury removal for PRB only as a function of UBC is much more steep than for the coal blends, and has a zero y-intercept. Coal blending indeed enhances mercury removal by providing needed catalytic material (UBC), but coal blending also introduces a significant concentration of inert or less active material (i.e., alumina, silica, iron) that dilutes the concentration of sorbent material (i.e., calcium) in the baghouse filter cake. Thus, the enhancement of mercury removal by coal blending is less efficient than through combustion modifications, and the relationship between Hg removal and UBC for the coal blends has a non-zero y-intercept.



**Figure 14.** Hg removal versus UBC for PRB-only and coal blends.

## Sodium Tetrasulfide Injection

Sodium tetrasulfide ( $\text{Na}_2\text{S}_4$ ) decomposes into elemental ( $\text{S}^\circ$ ) and ionic ( $\text{S}^{2-}$ ) forms of sulfur when injected into the flue gas. In coal-fired flue gas, the  $\text{S}^\circ$  directly captures elemental mercury and the  $\text{S}^{2-}$  directly captures  $\text{HgCl}_2$ , both reactions forming  $\text{HgS}$  as a product, which is the most stable and non-toxic form of mercury in our environment. Figure 15 illustrates the results of injecting  $\text{Na}_2\text{S}_4$  ~2.0 seconds in front of a baghouse. As shown, complete removal of mercury was obtained while burning PRB coal, with only ~12 ppmv of  $\text{Na}_2\text{S}_4$  in the flue gas. The technology was also effective at removing mercury produced by bituminous coal (see Fig. 15). However, chlorine reduced the effectiveness of  $\text{Na}_2\text{S}_4$ -injection directly proportional to the concentration of chlorine in the flue gas<sup>2,4</sup>. This is not a problem for PRB coals however, which typically have very low chlorine content. In addition, sodium-tetrasulfide injection has been shown effective at removing mercury from Municipal Waste Combustors (MWC), where the concentration of chlorine in the flue-gas is much higher than in coal-fired boilers. In fact, there are 6 commercially operating MWC units that use sodium tetrasulfide injection to remove mercury from the stack effluent<sup>7</sup>.



**Figure 15.** Direct Hg removal by  $\text{Na}_2\text{S}_4$ -injection.

## CONCLUSIONS

There are vast differences among power plants, including coal type, particulate control equipment, wet and dry scrubbing technologies, and boiler efficiencies. The mechanisms governing mercury speciation are highly dependent on the specific configuration of each power plant. Therefore, a variety of solutions are needed to provide Hg-mitigation solutions to the entire fleet of coal-fired power plants in the United States. Solutions include coal blending, ash conditioning, designer sorbents, oxidizing agents, catalysts, and multi-pollutant controls. Novel solutions include Na<sub>2</sub>S<sub>4</sub>-injection for direct removal of elemental and oxidized mercury and combustion modifications.

## ACKNOWLEDGEMENTS

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